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Size Reduction of Clay Particles in Nanometer Dimensions

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Abstract

This research work focuses on combining ball milling and ultrasonication to produce nano-size clay particles. Our work also emphasizes on increasing the specific surface area of montmorillonite clay particles by reducing the particle size to nanometer dimensions. We have characterized the as-received clay particles by using particle size analysis based on laser diffraction and found that the size of the clay particles is not consistent and the particle size distribution is very broad. However, after the unique treatment and processing, the clay particles were obtained in nanometer dimensions with narrowed particle size distribution.

Introduction

Particle size is not only a crucial parameter for polymer nanocomposites but also it plays a vital role in paints, pigments, inks, toners, chemicals, talc, drugs, pharmaceuticals, cosmetics, confectionery, chocolate liquor, etc. When the particle size gets reduced, the specific surface area is increased and it would increase the chemical activity of the inorganic materials[1]. When the high specific surface area of the particles is exposed to the polymer molecules, various properties[2,3] of the polymer nanocomposites are changed. Ball milling[4] is a widely used technique for particle size reduction. But the problem of agglomeration[5] is always there when it is in dry powder form. One of the main mechanical effects caused by the ultrasonication[6,7] is the disaggregation and deagglomeration of the particle assembly. Cavitation[7] is the important phenomenon in ultrasonication. A combination of ball milling and ultrasonication can lead to an effective particle size reduction.

Experimental Details

Cloisite-15A (Southern Clay Products Inc, Texas) is the organophilic montmorillonite clay used in our study. Glass balls in 3 and 5 mm, stainless steel balls in 5 and 8 mm were also used. Thumblers tumbler (Tru-Square metal products, WA) was used for ball milling. Ultrasonic Processor CPX 750 (Cole-Parmer Instruments, IL) was used for ultrasonication process. Particle size analyzer-Mastersizer 2000 (Malvern Instruments), Scanning Electron Microscope JSM 5610 were used to characterize the particle size.

Thumblers tumbler is a steel hexagon barrel with removable rubber lining and it is 9 cm in diameter and 8 cm in depth. A glass bottle, 5.5 cm in height and 2.5 cm diameter, is used inside the tumbler for the ball milling of clay. Effect of the different materials (glass and stainless steel) and different sizes (3mm, 5mm, 8mm) of balls on particle size reduction and distribution were studied. The milled particles were dispersed in xylene. Again ultrasonication was done on milled particles in xylene. An investigation on the amplitude, pulsation rate and time of the ultrasonication process was done with respect to particle size distribution and the optimum conditions in our laboratory were determined. Particle size analyzer was used to characterize the nanoparticles based on the principles of laser diffraction and morphological studies.

RESULTS AND DISCUSSION

The speed of the tumbler was maintained at 20 rpm in the ball milling operations. The slow speed is preferred in order to increase the possibility of the balls making contact with many particles; hence the impact energy is even and the centrifugal forces would not overcome gravity. The ratio of balls-to-clay particles in the tumbler media was 100:2.5 (grams) and it was allowed to run for 24 hours. 3 mm glass balls are found to give better results than the other balls used.

Kinetic Energy (K.E.) produced by a single ball = ½ (mv^2), where m is the mass of the ball and v is the velocity of the tumbler. The total kinetic energy is approximately the same for all the types of balls used even though they are different in size and nature (Table. 1). In the case of 3 mm glass balls, which have higher surface area, more contact with the particle occurs. When the glass bottle is rotating inside the tumbler, because of its lower mass (0.0363 gm), more number of balls reaches the maximum height, hits the top surface of the bottle and fell down. When the balls reach the bottom surface of the bottle and accelerates (i.e.) at h=0, all the potential energy is converted to kinetic energy. K.E is considered to be acting on the defects (internal pore, surface cracks, micro cracks and surface fissure) in the particles, which ultimately results in particle size reduction.

Types of balls	Mass of a Single ball (kg)	K.E produced by a Single ball (Joules)	No of balls in 100 grams	Total K.E (Joules)
3 mm glass balls	0.0363×10^{-3}	2.02×10^{-6}	2754	5563.08×10^{-6}
5 mm glass balls	0.142×10^{-3}	7.89×10^{-6}	704	5554.56×10^{-6}
5 mm s.steel balls	0.432×10^{-3}	2.4×10^{-5}	231	5544×10^{-6}
8 mm s.steel balls	1.069×10^{-3}	5.99×10^{-5}	94	5630×10^{-6}

Table 1 Total kinetic energy produced by different types of balls

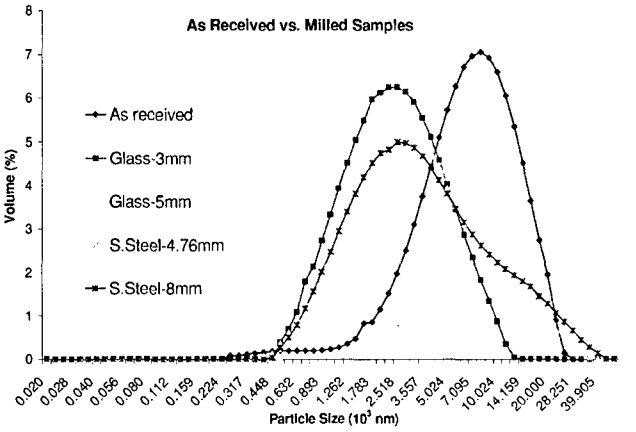

Figure 1. Particle Size Distribution Curves for the As-received and milled particles

The Particle Size Distribution (PSD), Specific Surface Area (SSA), Surface Weighted Mean (SWM) and Volume Weighted Mean (VWM) of as-received particles and ball-milled particles were determined using the Particle Size Analyzer. In a particle size distribution with a lot of fine particles, the SWM is very sensitive to the presence of finer particles. The VWM shows sensitivity to the presence of coarser particles. Thus, the direct use of as-received clay particles is not considered suitable for these applications of nanotechnology. So we decided to reduce the particle size and to narrow the size distribution by a combination of ball milling and ultrasonication techniques.

Properties	As-received nano-clay particles
PSD	0.02 to 2000 μm
SSA	1.22 m^2/g
SWM	4.9 μm
VWM	8.451 μm

Table II Properties of the As-received clay particles

Properties	Milled Samples (Effect of different types of balls on the particles)			
	3mm-Glass balls	*5mm-Glass balls*	*5mm-S.Steel balls*	*8mm-S.Steel balls*
PSD	0.63 to 14μm	0.35 to 41μm	0.44 to 50μm	0.44 to 55μm
SSA	2.92m^2/g	2.55m^2/g	2.2m^2/g	2.35m^2/g
SWM	2.052m^2/g	2.348m^2/g	2.724m^2/g	2.548m^2/g
VWM	3.172m^2/g	4.818m^2/g	5.830m^2/g	5.762m^2/g

Table III Effect of different types of balls on the As-received clay particles

Dry particles usually consist of aggregates and agglomerates that must be dispersed in xylene to produce individual units of the particle. When the particles were dispersed in xylene, there was a drastic change in the particle size and particle size distribution. The PSD, SSA, SWM, and VWM of the ball-milled clay particles dispersed in xylene are 0.5 μm to 33.570 μm, 36.8 m^2/g, 0.163 μm, and 1.022 μm respectively.

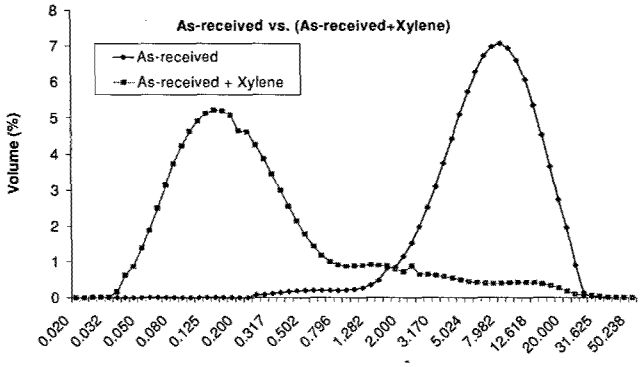

Figure 2. Particle Size Distribution curves for the As-received and milled particles.

Ultrasonication was done on the milled particles in xylene. The particles in xylene are considered the nuclei for the cavitation of bubbles. The high energy produced due to the collapse of bubbles at very high temperature was responsible for breaking the particles. The so-generated shock waves can cause the particles to collide against one another with great force. Since these are same charged particles, problem of agglomeration is greatly reduced. An investigation on the amplitude, pulsation rate and time of the ultrasonication process was done with respect to particle size distribution. Amplitude is directly proportional to the intensity, which is a measure of amount of energy available per unit volume of liquid. Hence as the amplitude increases, a higher energy is imparted to the cavitation bubble giving rise to greater intensity of the energy released in the implosion of that bubble. When the amplitude is increased from 80% to 90%, with pulse rate 5 sec. on and 5 sec. off, the SSA increases from 35.38m^2/g to 46.98m^2/g in 4 hours.

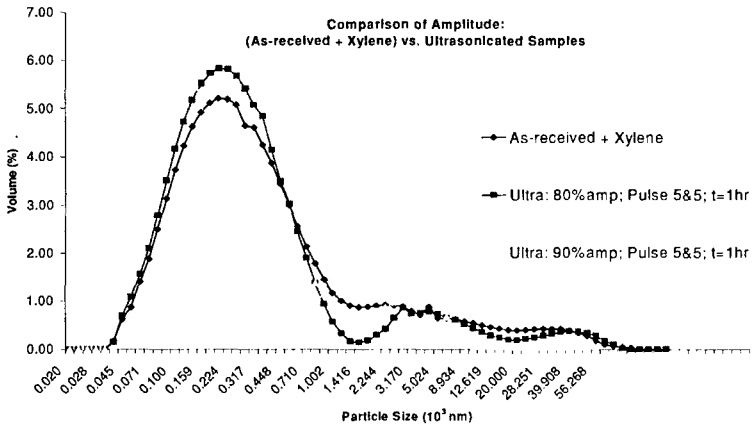

Figure 3.1 - Particle Size Distribution curves showing that higher amplitude is better (1 hour ultrasonication time)

The particle size distribution curve (span) becomes narrowed for the 90% amplitude curves compared with other curves (Fig 3.1 and Fig 3.2). The span expresses the width of the distribution curve regardless of the actual size of the material.

Time is another vital factor. The longer the time allowed for ultrasonication, the better the results of particle size reduction. When the ultrasonication time is changed from 15 min. to 1 hour and to 4 hours, the SSA increases from 38 m^2/g to 45.4 m^2/g and to 46.9 m^2/g respectively. The PSD of the treated samples also decreased accordingly. When the pulsation rate is changed from 5 sec. on and 5 sec. off to 8 sec. on and 4 sec. off, for 4 hours, the SSA increases from 35.5 m^2/g to 49.5 m^2/g. The span is also greatly reduced which indicates narrower particle size distribution (Fig 4).

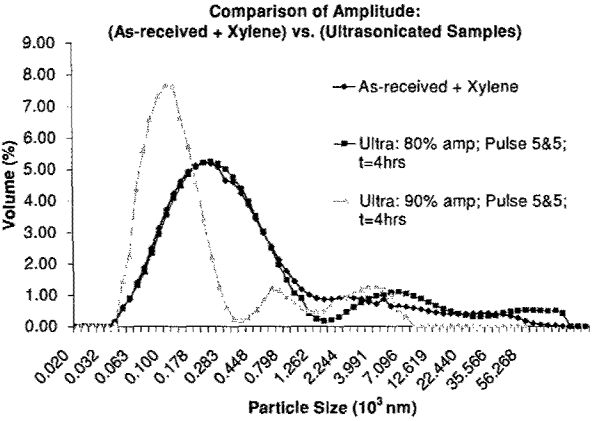

Figure 3.2 - Particle Size Distribution curves showing that higher amplitude is better (4 hours ultrasonication time)

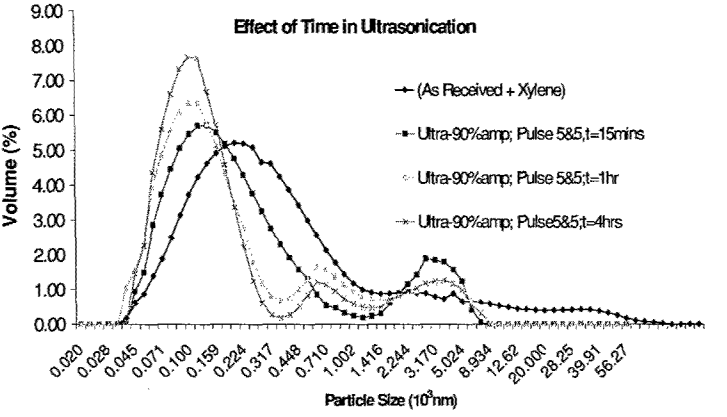

Figure 4 - Particle Size Distribution curves showing that when the ultrasonication time is increased, particle size and the span gets decreased.

The treated clay particles (after ball milling, dispersed in xylene and ultrasonication) were obtained in nanometer dimensions. Table IV summarizes the PSD, SSA, SWM and VWM of the clay particles before and after processing;

Parameters	As-received clay particles	Reduced size clay particles
PSD	0.02 μm to 2000 μm	50 nm to 350 nm
SSA	1.22 m^2/g	48.2 m^2/g
SWM	4.9 μm	128 nm
VWM	8.451 μm	650 nm

Table 1V As-received clay particles Vs. Reduced size clay particles

Conclusion

The optimum conditions for the ultrasonication process in our laboratory were determined; 90% amplitude, 8 second on and 4 second off pulsation rate, and 4 hours. The processed clay particles were obtained in nanometer dimensions. The average reduced particle size range is from 50 nm to 350 nm, average specific surface area is dramatically increased to 48.2 m^2/g, average surface weighted mean and average volume weighted mean are drastically decreased to 128 nm and 650 nm respectively.

Acknowledgements

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